

PATENT SPECIFICATION

(11) 1 348 146

1 348 146

- (21) Application No. 15270/71 (22) Filed 17 May 1971
 (23) Complete Specification filed 8 May 1972
 (44) Complete Specification published 13 March 1974
 (51) International Classification C08G 17/015
 (52) Index at acceptance
 C03R 3D13 3D2E 3N1 3P4
 (72) Inventors PETER FREDERICK JACKSON and JAMES ANGUS
 WILSON REID



(54) POLYESTERS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of highly polymeric polyesters of aromatic dicarboxylic acids and dihydric alcohols.

Highly polymeric polyesters of aromatic dicarboxylic acids and dihydric alcohols are known to be useful thermoplastic materials capable of conversion to films, fibres and moulded articles having a desirable combination of physical and chemical properties. Examples of such polyesters are those prepared, for example, from terephthalic acid or 1,2-di(*p*-carboxyphenoxy)ethane and ethylene glycol or butane-1,4-diol or 1,4-dihydroxymethylcyclohexane.

Many processes have been proposed for the production of these polyesters but in general they proceed via the formation of the bis(dihydric alcohol)ester of the aromatic dicarboxylic acid and the polycondensation of this intermediate to highly polymeric polyester with loss of dihydric alcohol by heating in a molten state under reduced pressure. The bis ester may be formed, for example, by reaction of the aromatic dicarboxylic acid or of an ester-forming derivative thereof, for example a dialkyl ester, with the dihydric alcohol, or by reaction of the dicarboxylic acid with an ester-forming derivative of the alcohol, for example, ethylene oxide or ethylene carbonate in the case of ethylene glycol. The process of reacting the acid with the dihydric alcohol is generally referred to as direct esterification, whereas the reaction of dialkyl ester with the dihydric alcohol is generally referred to as transesterification.

So as not to modify, dilute or lose the highly desirable characteristic properties of the highly polymeric polyesters of dihydric alcohols and aromatic dicarboxylic acids, it is preferred that the polycondensable material consist substantially entirely of one or more bis(dihydric alcohol) esters of aromatic dicarboxylic acids. However, the presence of a small concentration of other polycondensable material may be tolerated, if desired, for example to improve dyeability. For example, up to about 5 mole % of the dihydric alcohol moiety in the bis ester or esters may be replaced by at least one other polycondensable dihydroxy compound and/or up to about 5 mole % of the aromatic dicarboxylic acid moiety may be replaced by at least one other dicarboxylic acid. Up to about 5 mole % of the polycondensable mixture may also consist of other mono- or polyfunctional material, if desired. However, it is usually preferred that at least 85 mole %, and preferably at least 95 mole %, of the polycondensable mixture consists of bis(dihydric alcohol) ester of aromatic dicarboxylic acid or an oligomer thereof.

Both the process of forming the intermediate and its conversion to highly polymeric polyester by polycondensation are aided by the use of catalysts, which are generally metal compounds. In most conventional processes, different catalysts are used for the preparation of the bis(dihydric alcohol)ester intermediate and for the polycondensation, and the present invention provides an improved process for the polycondensation stage.

British Patent No. 1,046,831 describes a process for the production of highly polymeric linear polyesters of aromatic dicarboxylic acids by the catalytic polymerisation of a bis(ω -hydroxyalkyl)ester or bis(hydroxycycloalkyl)ester of the aromatic dicarboxylic acid, wherein there is present during the polymerisation at least 0.05%.

[Price 25p]

based on the weight of the dialkyl ester of the aromatic dicarboxylic acid, of certain specified organo-phosphorus compounds. The polymerisation is catalysed in conventional manner, for example with metallic compounds such as antimony trioxide.

British Patent No. 1,013,573 describes a polyester composition comprising:—

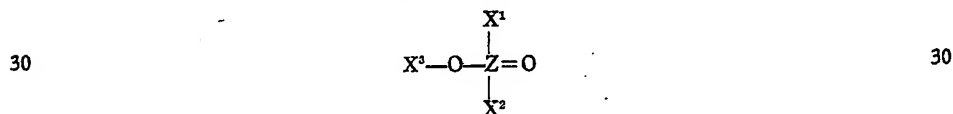
- 5 (1) a highly polymerised polyester derived from a difunctional acid component comprising at least 80 mole % of terephthalic acid and a dihydric alcohol component comprising at least 75 mole % of a polymethylene glycol or an alicyclic glycol; and
 10 (2) 0.1—20 mole % (based on the difunctional acid component) of a defined additive which is a sulphonamide, phosphonate or phosphinate. The polyester is prepared in conventional manner, for example by a polycondensation reaction catalysed by a metallic compound, such as antimony trioxide, and the additive is added before, during or after the polycondensation reaction.

15 British Patent No. 1,155,005 describes a process which comprises in a first stage reacting a dicarboxylic acid or mixture of acids, at least 80 mole % of which is terephthalic acid, or a lower aliphatic ester thereof with a glycol to produce a diglycol ester of the dicarboxylic acid or its oligomer, and in a second stage polycondensing the diglycol ester or its oligomer to produce a polyester, wherein at least the second stage reaction is performed in the presence of:

- 20 (a) a cerium or lanthanum compound which is soluble in the diglycol ester of the dicarboxylic acid or its oligomer, and
 (b) a defined aralkylphosphonic acid or ester.

Published Dutch Patent Application No. 7,105,372 describes and claims:

25 A two-stage process for the production of highly polymeric polyesters by (1) transesterification of a mixture containing a dialkyl ester of an aromatic dicarboxylic acid and a dihydric alcohol and (2) subsequent polycondensation of the bis(dihydric alcohol) ester of the aromatic dicarboxylic acid formed, both stages being conducted in the presence of a catalytic system comprising a mixture of a metal salt containing a weakly acidic anion including oxide and a compound of the structure

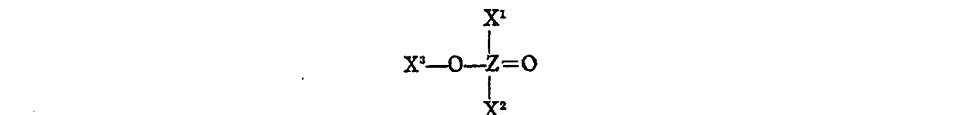


where X^1 is $-R$ or $-OR$, X^2 is R and X^3 is H or R , where R is a monovalent hydrocarbon group or a substituted derivative thereof, and Z is a Group VB element with an atomic number greater than 7.

35 We have now found that advantageous results may be obtained by the use of certain catalysts for the polycondensation reaction, in controlled quantities.

According to the present invention we provide a process for the production of highly polymeric polymer by the polycondensation of a polycondensable material at least 85 mole % of which consists of at least one bis(dihydric alcohol)ester of an aromatic dicarboxylic acid or an oligomer thereof, the polycondensation being effected in the presence, as catalyst, of a mixture of

- 40 (a) a metallic component which is selected from the salts of zinc, manganese or aluminium and zinc oxide, and
 (b) an organic component which is a compound of the structure



where Z is an element of Group VB of the Periodic Table having an atomic number greater than 7, X^1 $-R$ or $-OR$, X^2 is $-H$ or $-R$, and each R , which may be the same or different, is a hydrocarbon or substituted hydrocarbon group, in which process the amount of each component does not exceed 0.05% by weight of the polycondensable material.

(All references to the Periodic Table are to the version of the Periodic Table of the Elements printed inside the back cover of F A Cotton and G Wilkinson—Advanced Inorganic Chemistry, 2nd Edition (1966) Interscience Publishers, New York, London and Sydney).

5 Preferably, the amount of each component of the catalyst mixture does not exceed 0.05% by weight calculated on the basis of the dimethyl ester of the aromatic dicarboxylic acid. 5

10 Particularly suitable anionic ligands are the anions of weak acids, for example the anions of organic acids, particularly organic carboxylic acids, or the anions derived from enolisable β -diketones, for example acetylacetone. It is preferred that the metallic component is a salt of an aliphatic carboxylic acid, for example, an acetate. Zinc salts are particularly suitable and are therefore preferred.

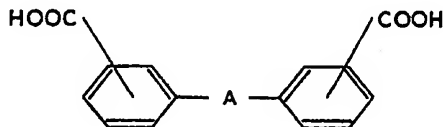
15 Preferred examples of the groups R in the organic component are alkyl, aryl, aralkyl and cycloalkyl groups, particularly alkyl.

20 Preferably R has 1 to 8 carbon atoms, as in methyl, ethyl, isomeric propyl, isomeric butyl, hexyl, cyclohexyl, octyl, and benzyl, for example. However, while it is preferred that R contains not more than eight carbon atoms, the presence in R of more than eight carbon atoms, as in decyl, dodecyl and naphthyl for example, is not excluded. One or more of the hydrogen atoms in R may be replaced, if desired, by other monovalent atoms or groups, for example halide, $-\text{NR}'\text{R}''$, $-\text{NO}_2$, $-\text{OOCR}'$, $-\text{COOR}'$, $-\text{COR}'$, $-\text{OR}'$, $-\text{SO}_2\text{OR}'$ or $-\text{OSO}_2\text{R}'$ where each of R' and R'' is hydrogen or a monovalent hydrocarbon radical, for example having 1 to 6 carbon atoms. It is preferable that the substituted groups (if any) are free of Zerewitinoff hydrogen if reaction of the catalyst with the polycondensable mixture is to be avoided. Preferably, Z is phosphorus, when the organic component will be a phosphinic acid or ester, or a phosphonic ester which may be a diester or a monoester containing one free acid group. Z may equally be arsenic, and the use of the heavier elements of Group VB is not excluded. 25

30 Very suitable phosphorus compounds are alkyl dialkyl-phosphinates or dialkyl alkylphosphonates in which the alkyl groups, which may be the same or different, contain from 1 to 6 carbon atoms.

35 We have found in particular that the combination of zinc acetate and a phosphinate or phosphonate is capable of catalysing the reaction at concentrations of zinc acetate not exceeding 0.02% by weight of the dimethyl ester of the aromatic dicarboxylic acid, to give polyesters having high lumirance and low yellowness. Preferably the concentration of each catalyst component does not exceed 0.02% by weight of the dimethyl ester.

40 The invention is especially applicable to the production of polyesters wherein the dicarboxylic acid is at least 80 mole % terephthalic acid, but other aromatic acids may also be used. Examples of other aromatic dicarboxylic acids include isophthalic acid and dinuclear dicarboxylic acids, for example those represented by the structure: — 40



45 where A is a direct link or a divalent atom or group which is inert under the reaction conditions. 45

50 Examples of dihydric alcohols that may be used are α,ω -polymethylene glycols, especially those having the structure $\text{HO}(\text{CH}_2)_x\text{OH}$ where x is from 2 to 10; branched aliphatic diols, for example 3,3,5-trimethylhexane-1,6-diol and neopentyl glycol; and alicyclic diols, for example 1,4-dihydroxymethylcyclohexane and 2,2,4,4-tetramethylcyclobutane-1,3-diol. Ethylene glycol and butane diol are preferred, especially the former. 50

55 The amount of catalyst used, calculated on the basis of weight of metallic component per cent weight of dimethyl ester of terephthalic acid (or equivalent if other acids are used) may be in the range 0.0001 to 0.05%, preferably 0.005 to 0.05%. The amount of organic component is preferably in the molar ratio to metallic component of 1:1 to 2:1. 55

With the use of the catalyst in these concentrations, rapid reactions may be achieved. Moreover, with the use of many of the catalysts in the process of our invention the clarity of the polyester melt has been observed to be better than that of high molecular weight polyesters obtained from many processes using conventional catalyst systems, for example based on metal acetates only and metal oxides.

It is an advantage of our process that the metallic component and the organic component, as defined above, may be the sole essential ingredients of the catalyst and it is unnecessary to add further catalysts such as antimony trioxide.

The polycondensable material may be produced in conventional manner by direct esterification or by transesterification. It is preferred that the polycondensable material is produced by direct esterification of the aromatic dicarboxylic acid with the dihydric alcohol.

Conventional reaction conditions may be used for the polycondensation reaction and other additives may be included before, during or after the reaction, for example, for delustering, stabilising, pigmentation and/or otherwise modifying the high molecular weight polyester product.

The invention is now illustrated by the following Examples.

Luminance (L) and yellowness (Y), when measured, were determined using a "Colormaster" differential Colorimeter manufactured by the Manufacturers Engineering and Equipment Corporation.

Two general polymerisation procedures were employed. In both methods, a polymerisation vessel was charged with bis(2-hydroxyethyl) terephthalate, which had been prepared in conventional manner either by transesterification of dimethyl terephthalate and ethylene glycol or by direct esterification of terephthalic acid with ethylene glycol. Polycondensation was then carried out as described below.

In method A, a glass polycondensation vessel was used which was fitted with a nitrogen inlet dipping below the level of the reactants, thereby effecting agitation. There was also provision of a vacuum offtake and condensing arrangements for volatile materials.

In method B, a stainless steel autoclave was used, which was provided with a double helical metal stirrer.

In both methods, titanium dioxide was added if delustred polymer was required. The temperature was then raised to 280° C. Pressure within the vessel was reduced to 0.5 mm of mercury absolute over a period of 30 minutes and heating was continued at 285° C. for 3 hours in the glass vessel or 1½ hours in the steel vessel. The polymeric reaction product was extruded onto chill-cast rollers and the intrinsic viscosity (I.V.) and L and Y values were measured.

Intrinsic viscosity was determined from relative viscosity measured in 1% solution in *o*-chlorophenol at 25° C.

Abbreviations: Me=methyl, et=ethyl, iPr=isopropyl, Ph=phenyl, Ac=acetate, Acac=acetylacetonate.

Examples 1—7.

A series of polymers were prepared by procedure A with 0.015% by weight (based on dimethyl terephthalate) of zinc acetate dihydrate and various phosphorus compounds. Results are summarised in the following table.

Example No.	Phosphorus Compound	Moles of Phosphorus compound per mole zinc compound	IV	L	Y
1	Me(Ph)P(O)OMe	2	0.49	78	11
2	Me(Ph)P(O)OMe	1	0.52	85	7
3	Me(Ph)P(O)OH	2	0.57	82	12
4	Me(Ph)P(O)OH	1	0.55	78	16
5	Me ₂ P(O)OH	2	0.55	77	12
6	Me ₂ P(O)OH	1	0.57	84	10
7	Me ₂ P(O)OMe	1	0.58	80	18

Examples 8—13.

A series of polymers were prepared using procedure A with 0.025% by weight (based on dimethylterephthalate) of manganese acetate with various phosphorus compounds. Results are summarised in the following table.

Example No.	Phosphorus Compound	Moles of Phosphorus compound per mole manganese compound	IV	L	Y
8	(EtO) ₂ P(O)Me	2	0.52	89	14
9	(iPrO) ₂ P(O)Me	1	0.50	81	22
10	Me(Ph)P(O)OMe	2	0.50	87	8
11	Me(Ph)P(O)OMe	1	0.54	87	13
12	Me ₂ P(O)OH	1	0.49	82	17
13	Me ₂ P(O)OMe	1	0.56	81	24

Examples 14—18.

A series of polymers were prepared using procedure B with 0.015% by weight (based on dimethylterephthalate) of zinc acetate dihydrate and various phosphorus compounds. In all cases 0.38% by weight of titanium dioxide was added as a delustrant. Results are summarised in the following table.

Example No.	Phosphorus Compound	Moles of Phosphorus compound per mole zinc compound	IV	Colour
14	$\text{Me}_2\text{P}(\text{O})\text{OH}$	1	0.79	White
15	$\text{Ph}_2\text{P}(\text{O})\text{OH}$	2	0.76	"
16	$(\text{EtO})_2\text{P}(\text{O})\text{Et}$	2	0.76	"
17	$(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{Ph}$	2	0.70	"
18*	$\text{MePhP}(\text{O})\text{OMe}$	2	0.62	"

*Zinc acetate replaced by zinc oxide (0.0055% by weight, calculated on the basis of dimethyl terephthalate).

Examples 19 and 20.

A series of polymers were prepared using procedure B with aluminium compounds and various phosphorus compounds as catalysts. In each case 0.5% by weight of titanium dioxide was added as a delustrant. Results are shown below.

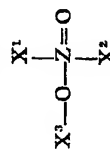
Example No.	Phosphorus Compound	Metal Compound	% weight of metal salt based on dimethyl terephthalate	Moles of Phosphorus Compound per mole Aluminium compound	IV	Colour
19	$\text{Me}_2\text{P}(\text{O})\text{OH}$	$\text{Al}(\text{AcAc})_3$	0.036	3	0.72	White
20	$(\text{MeO})_2\text{P}(\text{O})\text{Me}$	$\text{Al}(\text{AcAc})_3$	0.036	3	0.69	"

Example 21.

Polymer was made using procedure B with 0.015% by weight (based on dimethyl terephthalate) of zinc acetate dihydrate, and two moles of dimethylarsinic acid per mole of zinc salt. 0.38% by weight of titanium dioxide was added as a delustrant. White polymer was obtained with an intrinsic viscosity of 0.72.

WHAT WE CLAIM IS:—

1. A process for the production of highly polymeric polymer by the polycondensation of a polycondensable material, at least 85 mole % of which consists of at least one bis(dihydric alcohol) ester of an aromatic dicarboxylic acid or an oligomer thereof, the polycondensation being effected in the presence, as catalyst, of a mixture of
 - (a) a metallic component which is selected from salts of zinc, manganese or aluminium and zinc oxide, and
 - (b) an organic component which is a compound of the structure



5

10

15

15

wherein Z is an element of Group VB of the Periodic Table having an atomic number greater than 7, X¹ is —R or —OR, X² is —R, X³ is —H or —R, and each R, which may be the same or different, is a hydrocarbon or substituted hydrocarbon group, in which process the amount of each component does not exceed 0.05% by weight of the polycondensable material.

2. A process as claimed in claim 1 in which the amount of each component does not exceed 0.05% by weight calculated on the basis of the dimethyl ester of the dicarboxylic acid.

3. A process as claimed in claim 1 or claim 2 which the metallic component includes an anion of a weak acid.

4. A process as claimed in claim 3 in which the anion is derived from an organic carboxylic acid or an enolisable β -diketone.

5. A process as claimed in claim 4 in which the anion is an aliphatic carboxylate.

6. A process as claimed in any one of the preceding claims in which the metallic component is a zinc salt.

7. A process as claimed in any one of the preceding claims in which the groups R in the organic component are each alkyl, aryl, aralkyl or cycloalkyl, having from 1 to 8 carbon atoms.

8. A process as claimed in claim 7 in which each group R is alkyl.

9. A process as claimed in any one of the preceding claims in which the organic component is a phosphinic acid or ester, or a phosphonic ester.

10. A process as claimed in any one of the preceding claims in which the molar ratio of organic component to metallic component is in the range 1:1 to 2:1.

11. A process as claimed in any one of the preceding claims in which the amount of metallic component, calculated on the basis of the dimethyl ester of the dicarboxylic acid, is 0.0001 to 0.05% by weight.

12. A process as claimed in any one of the preceding claims in which the catalyst is a mixture of zinc acetate and an alkyl phosphinate or phosphonate, and the amount of zinc acetate, calculated on the basis of the dimethyl ester of the dicarboxylic acid, does not exceed 0.02% by weight.

13. A process as claimed in any one of the preceding claims in which the catalyst consists of the metallic component and the organic component as sole essential ingredients.

14. A process as claimed in any one of the preceding claims in which the dicarboxylic acid component of the polycondensable material is terephthalic acid.

15. A process as claimed in any one of the preceding claims in which the dihydric alcohol component of the polycondensable material is ethylene glycol.

16. A process as claimed in any one of the preceding claims in which the polycondensable material has been prepared by direct esterification.

17. A process as claimed in claim 1 for the production of highly polymeric polymer substantially as described and with reference to any one of the Examples.

18. A highly polymeric polymer when produced by the process of any one of the preceding claims.

D. PRICE.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1974.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.